

# DIFFUSIVITY OF Ga AND Al ADATOMS ON GaAs(001)

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The diffusivity of Ga and Al adatoms on the  $(2\times 4)$  reconstructed GaAs(001) surface are evaluated using detailed *ab initio* total energy calculations of the potential energy surface together with transition state theory. A strong diffusion anisotropy is found, with the direction of fastest diffusion being parallel to the surface As-dimer orientation. In contrast to previous calculations we identify a short-bridge position between the two As atoms of a surface dimer as the adsorption site for Al and Ga adatoms.

## 1 Introduction

Heteroepitaxy of GaAs and AlAs on (001) oriented substrates has been successfully applied to create structures of reduced dimensionality. In spite of the considerable progress in experimental studies the knowledge of the underlying microscopic processes is rather poor. For example, even for a key process like the Ga adatom diffusion on GaAs(001), the experimentally derived values for the activation energy<sup>1,2</sup> scatter significantly (between 1.1 and 4.0 eV) and the very basic question “which is the direction of fastest diffusion on GaAs(001)?” has not yet been answered, unambiguously. A similar lack of understanding exists with respect to the question of how the diffusion properties of Al and Ga adatoms differ. This is crucial for controlling the growth of high quality GaAs/AlAs quantum devices.

In this paper we present calculations of the diffusivities (activation energies as well as pre-exponential factors) of Ga and Al adatoms on the flat GaAs(001) surface using density functional total energy calculations.

## 2 Method

Typically the rate constant for adatom hops between neighboring sites is by orders of magnitude smaller than the highest phonon frequencies. Therefore, an *ab initio* molecular dynamics simulation is not a practicable approach to evaluate the diffusivity. It is clearly more appropriate to evaluate the Born-Oppenheimer potential energy surface (PES) and to analyse its properties. Our study of the diffusivity proceeds in three steps. At first we determine the PES using density functional theory and the generalized gradient approximation<sup>3</sup> for the exchange and correlation potential. This calculation identifies the local minima  $\{\mathbf{A}_I\}$  of the PES. We then apply transition state theory<sup>4</sup> (TST)

to determine the individual jump rates  $\Gamma_{I,J}$  between different sites  $\mathbf{A}_I$  and  $\mathbf{A}_J$ . In a third step we use a random walk model which assumes uncorrelated jumps between the sites  $\{\mathbf{A}_I\}$  to obtain the diffusivities in the two orthogonal directions,  $[110]$  and  $[\bar{1}10]$ . These are the main axes of the diffusion tensor according to the symmetry of the considered surface structure.

In TST the jump rate between two sites  $\mathbf{A}_I$  and  $\mathbf{A}_J$  is

$$\Gamma_{I,J} = \Gamma_{I,J}^0 \exp(-\Delta E/k_B T) \quad , \quad (1)$$

where  $\Delta E$  is the difference between the energies of the adatom at the site  $\mathbf{A}_I$  and at the saddle point between the sites  $\mathbf{A}_I$  and  $\mathbf{A}_J$ . To find these sites and the energy barrier  $\Delta E$ , we calculate the PES for a diffusing adatom:

$$E^{\text{PES}}(X_1, Y_1) = \min_{Z_1, \{\mathbf{R}_i\}_{i=2, \dots, N}} E(\{\mathbf{R}_i\}) \quad . \quad (2)$$

The set  $\{\mathbf{R}_i\}$  describes the positions of the atoms where  $X_1$ ,  $Y_1$  and  $Z_1$  are the coordinates of the adatom parallel and perpendicular the surface, respectively.  $E(\{\mathbf{R}_i\})$  is the total energy of the surface with an adatom.

The pre-exponential factor  $\Gamma_{I,J}^0$  is determined within the harmonic approximation of TST<sup>5</sup>:

$$\Gamma_{I,J}^0 = \frac{1}{\sqrt{4\pi^2 m_{\text{ad}}}} \sqrt{\frac{\det|K_I|}{\det|K'_S|}} \quad . \quad (3)$$

$K_I$  and  $K'_S$  are the force constant matrices for the adatom at the site  $\mathbf{A}_I$  and at the saddle point between  $\mathbf{A}_I$  and  $\mathbf{A}_J$ . Both matrices contain the force constants for  $\mathbf{R}_1$  and for the coordinates  $\mathbf{R}_i$  of substrate atoms next to the adatom. According to the TST,  $K'_S$  does not contain the mode perpendicular to the transition plane between  $I$  and  $J$ .

### 3 Results

We assume in our study that the surface is reconstructed with the  $(2 \times 4) \beta 2$  structure which consists of rows of two As dimers and two missing dimers in the topmost layer. This structure is found to be present under typical growth conditions<sup>6</sup> and is also a structure of lowest surface energy.<sup>7</sup>

Our calculations show that for both adatom species Al and Ga there exist two sheets of the PES which are relevant for diffusion. The occurrence of several sheets is not too surprising because in the combined configuration space of the adatom and the substrate there may be several saddle points between

two local minima  $\mathbf{A}_I$  and  $\mathbf{A}_J$ . Accordingly the PES as defined in Eq. (2) does not need to be a unique function.

The two sheets of the PES differ in the way the adatom interacts with the surface As-dimers. Either the surface displays only small relaxations (in particular the dimer bonds remain intact) when the adatom diffuses across the surface or the adatom breaks a surface dimer and causes a strong relaxation. For most positions  $(X_1, Y_1)$  of the adatom the two PES are identical. The differences occur only around the the surface dimers and are caused by an energy barrier to break the dimers.

If the adatom does not break the surface dimers (see Fig. 1(a)) the long-bridge position  $\mathbf{A}_1$  between surface dimers is the favoured site for adsorption. This agrees with previous calculations<sup>8</sup> which found a long-bridge position as the adsorption site. However, we find that the site of lowest total energy, i.e., the actual adsorption site, is the short-bridge position  $\mathbf{A}_4$  (Fig. 1(b)). If the adatom is adsorbed at this position the surface dimer is broken and the adatom forms directional bonds with the As atoms of the broken dimer. Such directional bonds are not formed when the adatom is located at one of the long-bridge sites  $\mathbf{A}_1$  or  $\mathbf{A}_2$  where the adatom does not break any surface bond. Therefore, the adatom can interact at an  $\mathbf{A}_1$  or  $\mathbf{A}_2$  site only with the completely filled dangling bonds of the As-dimers. Accordingly the adsorption energies at the long-bridge sites are by about 0.6 eV smaller than at the short-bridge sites ( $\mathbf{A}_3, \mathbf{A}_4$ ).

In order to obtain the diffusivity the jump rates on both sheets of the PES between the various sites of local total energy minima were combined by using a random walk model on a periodic lattice with inequivalent sites.<sup>9</sup> The resulting mobilities along the  $[110]$  and  $[\bar{1}10]$  direction are  $D_{[\bar{1}10]} = 0.015 \text{ cm}^2/\text{s} \exp(-1.2 \text{ eV}/k_B T)$  and  $D_{[110]} = 0.03 \text{ cm}^2/\text{s} \exp(-1.5 \text{ eV}/k_B T)$  for Ga adatoms and  $0.03 \text{ cm}^2/\text{s} \exp(-1.4 \text{ eV}/k_B T)$  and  $0.05 \text{ cm}^2/\text{s} \exp(-1.6 \text{ eV}/k_B T)$  for Al, respectively. These diffusion constants are significantly smaller than previously published values determined by *ab initio* total energy calculations.<sup>8</sup> This difference is due to the fact that the activation energy of diffusion is mainly determined by the energy needed to jump away from the adsorption site, which was not correctly identified in former investigations.

The calculated diffusion constants exhibit a pronounced anisotropy. As it is already obvious in Fig. 1, the barriers for diffusion between two adjacent  $\mathbf{A}_4$  sites are smaller along the  $[\bar{1}10]$  direction than along the  $[110]$  direction. Accordingly, diffusion is fastest along the  $[\bar{1}10]$  direction. Comparing the PES of Ga and Al adatoms we find no qualitative differences. But the PES for an Al adatom is more strongly corrugated and therefore it has higher diffusion barriers. This is a consequence of the larger adatom-As bond strength for Al

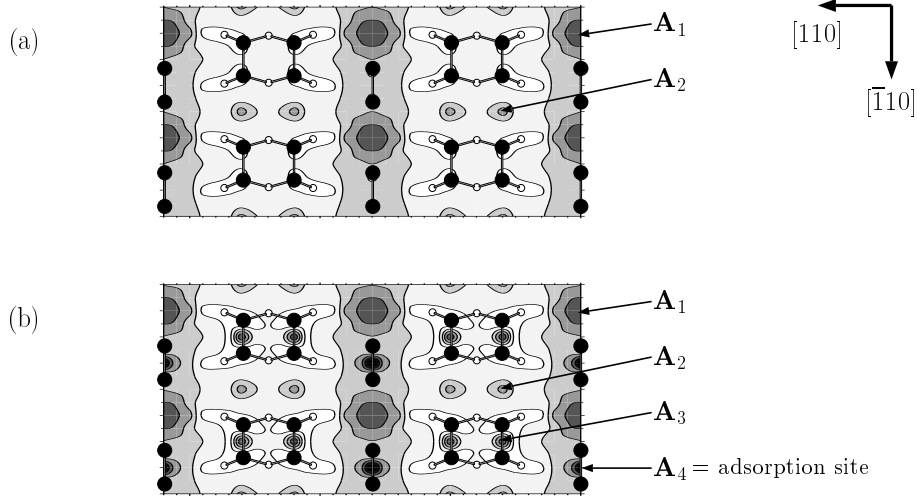


Figure 1: Potential energy surfaces for a Ga adatom on the GaAs(001)-(2x4)  $\beta_2$  surface. (a) PES sheet obtained when the As surface dimers remain intact. (b) PES sheet obtained when the surface dimers are broken by the adatom. The contour-line spacing is 0.3 eV. The atomic positions of the clean surface are indicated for atoms of the upper two layers and for the As-dimers in the third layer (As: filled circles, Ga: empty circles).

as reflected by the higher cohesive energy of AlAs compared to that of GaAs. Therefore, Al diffuses slower than Ga in spite of the fact that Al has a higher pre-exponential factor (see Eq. (3)), which is mainly caused by the lower mass of Al as compared to Ga.

## References

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